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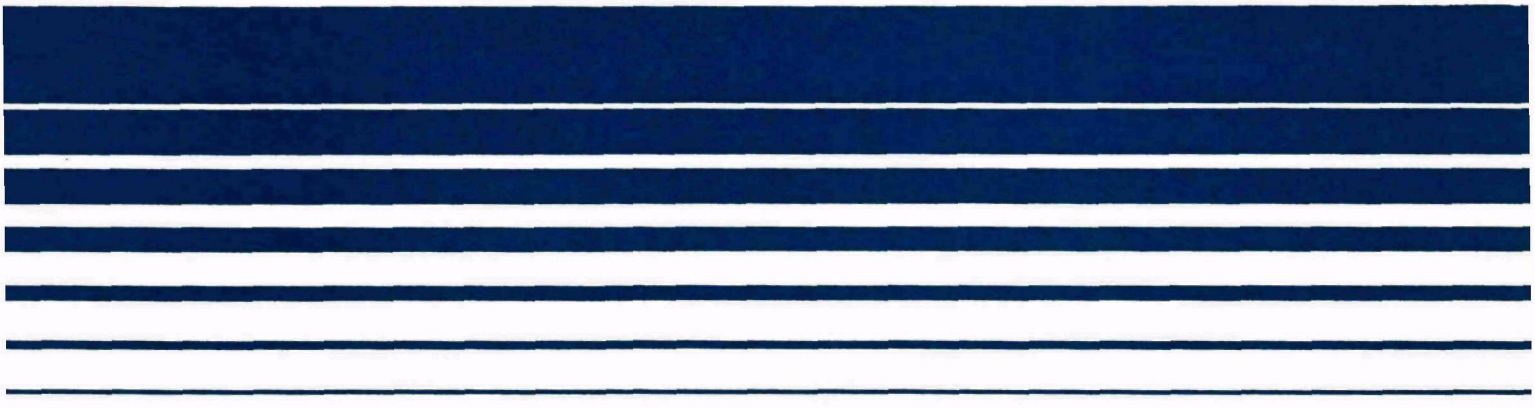
Urea Manufacture

Emission Test Report
Union Oil Company of California
Brea, California



REPORT ON PROCESS EMISSIONS TESTS AT THE UNION OIL COMPANY UREA MANUFACTURING FACILITY IN BREA, CALIFORNIA

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PREFACE

The work reported herein was performed by personnel from TRC Environmental Consultants, Inc. (TRC), Radian Corporation, the Union Oil Company, Brea, California, and the U.S. Environmental Protection Agency (EPA).

The scope of work, issued under EPA Contract No. 68-02-2820, Work Assignment No. 20, was under the supervision of the TRC Project Manager, Mr. Willard A. Wade III. Mr. Leigh Gammie of TRC served as Project Engineer and was responsible for summarizing the test and analytical data presented in this report. Sample analysis was performed at the TRC laboratory in Wethersfield, Connecticut under the direction of Mr. Samuel S. Cha.

Mr. John H.E. Stelling III of Radian was responsible for monitoring the process operations during the emissions testing program. Radian personnel were also responsible for preparing Section 3.0, Process Description and Operations, of this report.

Personnel of Union Oil Company, Brea, California, whose assistance and guidance contributed greatly to the success of this program include Mr. J.D. Swanburg, Process Superintendent - Central Plant Engineering, and Mr. Robert W. Waddell, Process and Control Superintendent.

Mr. Eric A. Noble, Office of Air Quality Planning and Standards, Industrial Studies Branch, EPA, served as Test Process Project Engineer and was responsible for coordinating the process operations monitoring.

Mr. Clyde E. Riley, Office of Air Quality Planning and Standards, Emission Measurement Branch, EPA, served as Technical Manager and was responsible for coordinating the emission test program.

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NOTE: Mention of trade names or commercial products in this publication does not constitute endorsement or recommendation for use by the United States Environmental Protection Agency.

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1.0 INTRODUCTION

1.1 Background

Section 111 of the Clean Air Act of 1970 charges the Administrator of the United States Environmental Protection Agency (EPA) with the responsibility of establishing Federal standards of performance for new stationary sources which may significantly contribute to air pollution. When promulgated, these standards of performance for new stationary sources (SPNSS) are to reflect the degree of emission limitation achievable through application of the best demonstrated emission control technology. Emisson data, collected from controlled sources in the particular industry of concern, provide a portion of the data base used by EPA to develop the SPNSS.

The EPA Office of Air Quality Planning and Standards (OAQPS) selected the Union Oil Company urea manufacturing plant in Brea, California, as a site for an emission test program. This plant produces feed and fertilizer grade urea, and is considered to employ process and emission control technology representative of modern urea solution formation and prilling processes.

EPA engaged TRC to conduct tests designed to characterize and quantify controlled emissions from the solids production (prill tower) and cooling processes. Figure 1-1 shows a flow diagram of the complete urea production process. Emission tests were performed during April 1980 at the outlet of one of the four prill tower scrubbers and at the inlet of the rotary drum cooler scrubber. These tests were performed during production of fertilizer grade urea.

1.2 Brief Process Description

This facility produces feed and fertilizer grade urea, utilizing one continuously operating prill tower. A flow diagram of the urea production process is shown in Figure 1-1. Concentrated urea melt from the urea solution

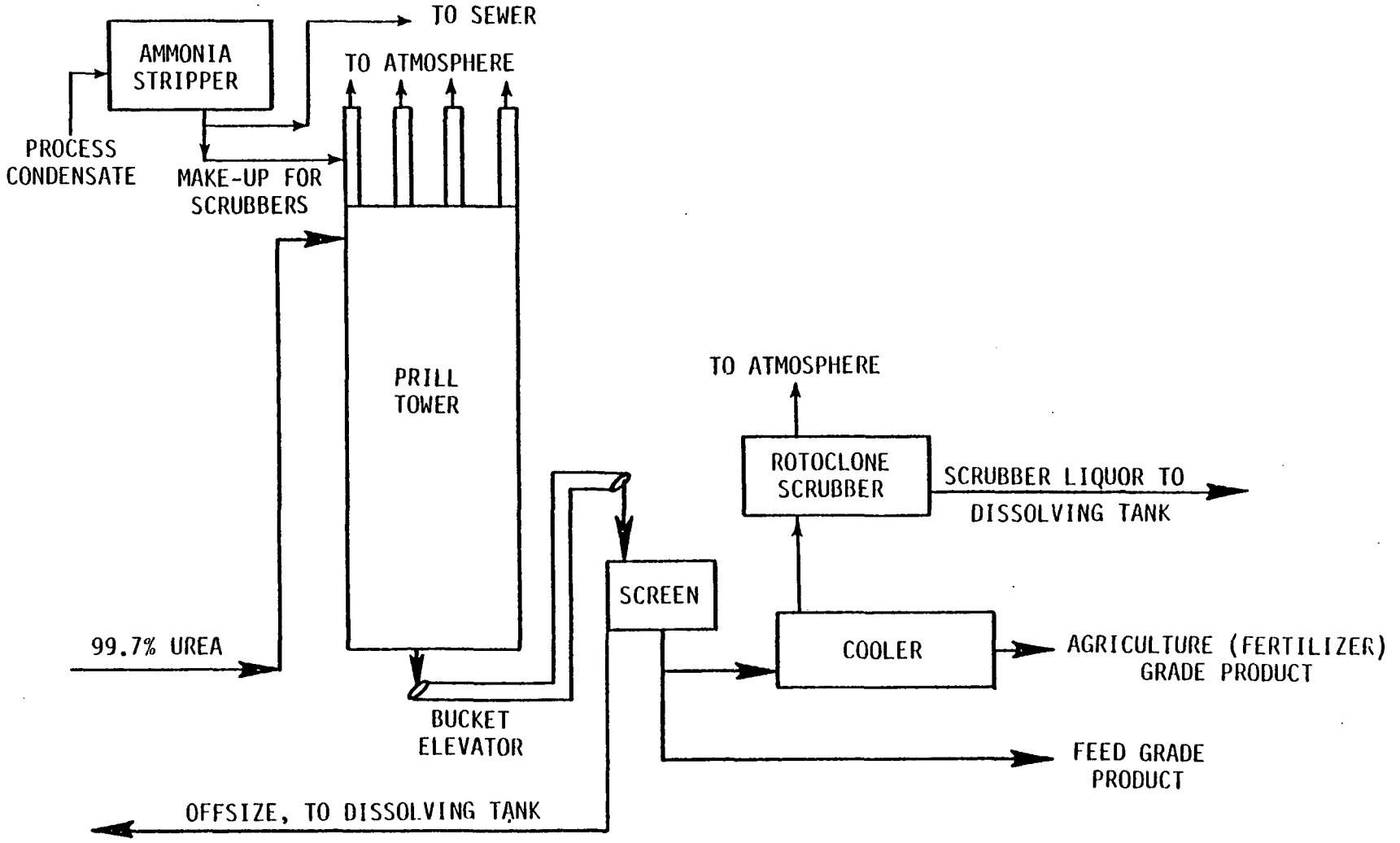

FIGURE 1-1 : UREA MANUFACTURING PROCESS FLOW DIAGRAM
UNION OIL COMPANY OF CALIFORNIA
BREA, CALIFORNIA

formation process is pumped to a rotating chamber at the top of the prill tower, from which the melt is sprayed downward against a countercurrent of ambient air drawn through the tower. The falling urea droplets solidify and the solid urea particles (prills) are removed from the bottom of the tower by a conveyor. The fertilizer-grade product is cooled in a rotary drum cooler and then transported to bulk storage; the feed product is transported directly to storage. The chemical processes for producing the two product grades are nearly identical. The prill tower operation is changed in order to produce the smaller feed grade prills. Approximately 370 tons of fertilizer grade urea can be produced per day at this plant.

The emissions control system used on the 150-foot high prill tower is a group of four scrubbers located at the top of the tower. The four scrubbers operate simultaneously and have a common sump and pump system for collecting and recycling the scrubbing liquor. Air flow through the rotary drum prill cooler is controlled by a rotoclone scrubber.

1.3 Emissions Measurement Program

The emissions measurement program was conducted on April 24, 25, and 28, 1980 at the Union Oil Company, urea manufacturing plant in Brea, California. The measurement program consisted specifically of the following:

1. Urea and ammonia in the outlet gas stream of the prill tower Northeast scrubber.
2. Urea and ammonia in the inlet gas stream of the prill cooler scrubber.
3. Urea, solids content, pH, and temperature of the inlet liquor of the prill tower Northeast scrubber.
4. Volumetric flowrates in the three prill tower scrubber outlets not tested for emissions.
5. Ambient air temperature and relative humidity during emission tests.

6. Prill tower Northeast scrubber pressure drop measurements during emission tests.

TRC personnel were responsible for collecting the above emissions data. Concurrently, Radian personnel were responsible for monitoring and recording pertinent process operation parameters. The chronology of the emissions tests is contained in the Daily Summary Logs in Appendix D.

The following sections of this report present the results of the fertilizer grade emissions tests (Section 2.0), process description (Section 3.0), location of sampling points (Section 4.0), and a discussion of the sampling and analysis methods (Section 5.0). Detailed descriptions of methods and procedures, field and laboratory data, and calculations are presented in the various appendices, as noted in the Table of Contents.

Appendix F.4 contains the results of audit sample analyses. Urea standards where prepared by EPA and then analyzed by TRC in accordance with EPA instructions in order to assess the accuracy of the urea analysis procedure.

Appendix F.5 contains the results of the cleanup evaluations performed on the sampling train equipment. The sampling train was assembled and charged as if ready to perform a test for urea and ammonia. The unexposed impinger contents were then recovered, prepared and analyzed according to procedure in order to establish background/contamination levels of urea from the sample collection equipment.

2.0 SUMMARY OF RESULTS

This section presents summary tables of results and narrative on the emissions testing conducted April 24-28, 1980, at the Union Oil Company urea manufacturing facility in Brea, California. Testing was performed on the gas stream exiting, and the liquor stream entering, one of the prill tower scrubbers; and on the gas stream entering the prill cooler scrubber.

Urea analyses were performed with the p-dimethylaminobenzaldehyde (PDAB) method (with preliminary distillation). Ammonia analyses were performed with the specific ion electrode (SIE) method. Both analysis methods are discussed in Section 5.0 and Appendices E and F.

2.1 Prill Tower Emission Test Results for Northeast Scrubber Outlet

Table 2-1 presents the urea and ammonia results for the emission test runs performed on the prill tower Northeast scrubber outlet gas stream. In accordance with instructions from the Technical Manager, the acid impinger urea analysis results are not included in the data shown in Table 2-1. As shown in Appendix F.1, the acid impinger urea analysis results indicate essentially no urea in the acid impingers. These results reflect the fact that, as discussed in Section 2.3, all the sampled urea is caught in the first two water impingers and in the probe.

2.2 Prill Cooler Scrubber Inlet Emission Test Results

Table 2-2 presents the urea and ammonia results for the emission test runs performed on the Rotary Drum Prill Cooler scrubber inlet gas stream. As with the prill tower scrubber data, the acid impinger urea analysis results are not included in the data shown in Table 2-2.

TABLE 2-1a (English Units)

SUMMARY OF UREA AND AMMONIA TESTS
ON GASES EXITING THE PRILL TOWER NORTHEAST SCRUBBER
ON APRIL 24-25, 1980
AT UNION OIL COMPANY, BREA, CALIFORNIA

Run Number	1	2	3	Average
Date	4-24-80	4-25-80	4-25-80	
Volume of Gas Sampled (DSCF)[a]	94.69	97.19	103.3	98.39
Stack Gas Flow Rate (DSCFM)[b]	13070	13730	13870	13560
Stack Temperature (^{o}F)	77	76	77	77
Percent Moisture	4.799	4.584	5.676	5.020
Percent Isokinetic	106.3	103.9	109.3	106.5
Production Rate (Tons/Hour)	12.0	12.5	12.3	12.3
Urea Data[c]				
Total Sample Weight (mg)	77.90	50.13	61.98	63.34
Grains/DSCF	0.01269	0.007959	0.009262	0.009932
Pounds/Hour	1.423	0.9366	1.101	1.154
Pounds/Ton	0.1186	0.0749	0.0895	0.0938
Ammonia Data[d]				
Total Sample Weight (mg)	172.4	195.0	375.5	247.6
Grains/DSCF	0.0281	0.0310	0.0561	0.0284
Pounds/Hour	3.149	3.644	6.668	3.304
Pounds/Ton	0.2624	0.1518	0.5421	0.2686

[a]Dry standard cubic feet @ 68^{o}F, 29.92 inches Hg.
[b]Dry standard cubic feet per minute.
[c]p-dimethylaminobenzaldehyde (with preliminary distillation) Analysis Method.
[d]Specific Ion Electrode Analysis Method.

TABLE 2-1b (Metric Units)

SUMMARY OF UREA AND AMMONIA TESTS
ON GASES EXITING THE PRILL TOWER NORTHEAST SCRUBBER
ON APRIL 24-25, 1980
AT UNION OIL COMPANY, BREA, CALIFORNIA

Run Number	1	2	3	Average
Date	4-24-80	4-25-80	4-25-80	
Volume of Gas Sampled (Nm^3)[a]	2.682	2.752	2.924	2.786
Stack Gas Flow Rate (Nm^3/Min)[b]	370.3	388.8	392.7	383.9
Stack Temperature (^oC)	25	24	25	25
Percent Moisture	4.799	4.584	5.676	5.020
Percent Isokinetic	106.3	103.9	109.3	106.5
Production Rate (Mg/Hour)	6.0	6.3	6.2	6.2
Urea Data[c]				
Total Sample Weight (mg)	77.90	50.13	61.98	63.34
mg/Nm^3	29.05	18.21	21.20	22.82
Kg/Hour	0.6458	0.4252	0.4998	0.5236
Kg/Mg	0.1076	0.0675	0.0806	0.0845
Ammonia Data[d]				
Total Sample Weight (mg)	172.4	195.0	375.5	247.6
mg/Nm^3	64.30	70.86	128.4	87.85
Kg/Hour	1.430	1.654	3.027	2.037
Kg/Mg	0.2383	0.2625	0.4882	0.3285

[a]Normal cubic meters @ 20°C, 760 mm Hg.
[b]Normal cubic meters per minute.
[c]P-dimethylaminobenzaldehyde (with preliminary distillation) Analysis Method.
[d]Specific Ion Electrode Analysis Method.

TABLE 2-2a (English Units)

SUMMARY OF UREA AND AMMONIA TESTS
ON GASES ENTERING THE ROTARY PRILL COOLER SCRUBBER
ON APRIL 28, 1980
AT UNION OIL COMPANY, BREA, CALIFORNIA

Run Number	1	2	3	Average
Date	4-28-80	4-28-80	4-28-80	
Volume of Gas Sampled (DSCF)[a]	50.68	46.92	51.52	49.71
Stack Gas Flow Rate (DSCFM)[b]	7696	7102	7733	7511
Stack Temperature (^{o}F)	127	127	125	126
Percent Moisture	2.991	3.336	3.270	3.199
Percent Isokinetic	105.1	105.5	106.4	105.7
Production Rate (Tons/Hour)	11.7	11.7	11.7	11.7
Urea Data[c]				
Total Sample Weight (mg)	5357	3780	4517	4551
Grains/DSCF	1.631	1.243	1.353	1.413
Pounds/Hour	107.6	75.67	89.65	90.96
Pounds/Ton	9.197	6.468	7.662	7.774
Ammonia Data[d]				
Total Sample Weight (mg)	21.70	31.88	36.40	29.99
Grains/DSCF	0.006607	0.01048	0.01090	0.009309
Pounds/Hour	0.4358	0.6382	0.7225	0.5993
Pounds/Ton	0.0372	0.0545	0.0618	0.0512

[a]Dry standard cubic feet @ 68^{o}F, 29.92 inches Hg.
[b]Dry standard cubic feet per minute.
[c]P-dimethylaminobenzaldehyde (with preliminary distillation) Analysis Method.
[d]Specific Ion Electrode Analysis Method.

TABLE 2-2b (Metric Units)

SUMMARY OF UREA AND AMMONIA TESTS
ON GASES ENTERING THE ROTARY PRILL COOLER SCRUBBER
ON APRIL 28, 1980
AT UNION OIL COMPANY, BREA, CALIFORNIA

Run Number	1	2	3	Average
Date	4-28-80	4-28-80	4-28-80	
Volume of Gas Sampled (Nm^3)[a]	1.435	1.329	1.459	1.407
Stack Gas Flow Rate (Nm^3/Min)[b]	218.0	201.1	219.0	212.7
Stack Temperature (^oC)	53	53	51	52
Percent Moisture	2.991	3.336	3.270	3.199
Percent Isokinetic	105.1	105.5	106.4	105.7
Production Rate (Mg/Hour)	5.9	5.9	5.9	5.9
Urea Data[c]				
Total Sample Weight (mg)	5357	3780	4517	4551
mg/Nm^3	3733	2845	3096	3224
Kg/Hour	48.85	34.35	40.70	41.30
Kg/Mg	8.280	5.822	6.900	7.000
Ammonia Data[d]				
Total Sample Weight (mg)	21.70	31.88	36.40	29.99
mg/Nm^3	15.12	23.99	24.95	21.35
Kg/Hour	0.1979	0.2897	0.3280	0.2719
Kg/Mg	0.0335	0.0491	0.0556	0.0461

[a]Normal cubic meters @ 20^oC, 760 mm Hg.
[b]Normal cubic meters per minute.
[c]p-dimethylaminobenzaldehyde (with preliminary distillation) Analysis Method.
[d]Specific Ion Electrode Analysis Method.

2.3 Sample Collection Efficiency at the Prill Tower Scrubber

Three emission tests runs were performed on the outlet of the Northeast scrubber atop the prill tower. One purpose of these tests was to provide information on the urea collection efficiency of the EPA Method 28 sampling train.

The impinger sequence used for these tests was as follows:

impingers 1 and 2 - deionized, distilled water

impingers 3 and 4 - 1N sulfuric acid

impinger 5 - empty

impinger 6 - silica gel

The probe wash, the contents of impinger 1, the contents of impinger 2, and the combined contents of impingers 3, 4, and 5 were analyzed individually for urea and ammonia at the TRC laboratories within 20 days of sample collection. Urea analysis was performed using the p-dimethylaminobenzaldehyde method with preliminary distillation. Ammonia analysis was performed using the specific ion electrode method.

The results of the component analyses for these three prill tower scrubber test runs are shown in Table 2-3. These data indicate that 70% of the urea in the sampled gas is retained by the probe and first water impinger, and the remaining urea is retained by the second water impinger. The ammonia data indicate that half the ammonia is retained by the water impingers and half by the acid impingers.

2.4 Volumetric Flowrates in the Prill Tower Scrubber Outlets

Velocity traverses were performed in the Southeast, Southwest, and Northwest scrubber outlets immediately before and after each emissions test run. The calculated flowrates resulting from these velocity traverses and from the

TABLE 2-3

UREA SAMPLING TRAIN COLLECTION EFFICIENCY RESULTS
UNION OIL COMPANY, BREA, CALIFORNIA

	Test Run		Probe Wash	Impinger 1	Impinger 2	Impingers 3,4,5	Total
Urea	1	milligrams	4.50	44.6	28.8	< 1.64*	77.90
		percent	5.8	57.3	36.9	0	100
	2	milligrams	4.83	31.8	13.5	< 1.58*	50.13
		percent	9.6	63.4	27.0	0	100
	3	milligrams	5.58	41.1	15.3	< 1.49*	61.98
		percent	9.0	66.3	24.7	0	100
	Average	milligrams	4.97	39.2	19.2	-	63.34
		percent	7.8	61.9	30.3	0	100
Ammonia	1	milligrams	5.43	72.6	26.9	67.5	172.43
		percent	3.1	42.1	15.6	39.2	100
	2	milligrams	2.83	50.1	40.1	102	195.03
		percent	1.5	25.7	20.6	52.2	100
	3	milligrams	3.10	110	63.3	199	375.40
		percent	0.8	29.3	16.9	53.0	100
	Average	milligrams	3.79	77.6	43.4	123	247.62
		percent	1.5	31.3	17.5	49.7	100

*Detection Threshold (0.010 absorbance reading). Urea standards were prepared with similar acid contents as these acid impinger samples.

Northeast scrubber emission tests are shown in Table 2-4. The total average flowrate through the entire prill tower (all four scrubber outlets) was approximately 49,900 dry standard cubic feet per minute.

2.5 Pressure Drop Measurements Across the Prill Tower Northeast Scrubber

Pressure drops across the prill tower Northeast scrubber were monitored periodically (but not recorded) during each emission test run. During these runs the pressure drop averaged approximately 2.5 inches water.

2.6 Scrubber Liquor Analysis Data

Scrubber liquor samples from the common inlet to the four prill tower scrubbers were collected approximately every hour during each prill tower emission test run. The liquor temperature was measured immediately after the sample was collected, and when the sample reached room temperature the pH was measured and recorded. After each emission test run, the samples taken during that run were combined into one composite sample. The composite samples were then analyzed for urea and undissolved solids. A summary of the analysis data is shown in Table 2-5.

2.7 Ambient Air Temperature and Relative Humidity Measurements

The temperature and relative humidity of the ambient air were measured periodically at the base of the prill tower during each emission test run. These data are presented in Table 2-6.

TABLE 2-4

PRILL TOWER SCRUBBER OUTLET FLOW RATES*
AT UNION OIL COMPANY, BREA, CALIFORNIA

Scrubber Outlet	Time	Run 1	Run 2	Run 3	Average
Northeast	During	13070	13730	13870	13560
Southeast	Before[a]	11258	11808	12609	11892
	After[b]	**	12609	12150	12379
	Average	11258	12208	12379	12135
Southwest	Before	10496	12645	12888	12010
	After	**	12888	12798	12843
	Average	10496	12766	12843	12426
Northwest	Before	11814	12076	12902	12264
	After	**	12902	12497	12699
	Average	11814	12489	12699	12481
Total Flow[c]		46600	51200	51800	49900

[a]Flow rates calculated from velocity traverses performed before the indicated runs.
[b]Flow rates calculated from velocity traverses performed after the indicated runs.
[c]Sum of during and average flow rates, rounded to the nearest 100 DSCFM.

* Dry standard cubic feet per minute @ 68°F, 29.92 inches Hg.
**Velocity traverse data invalid due to shut down of the prill tower.

TABLE 2-5

SUMMARY OF PRILL TOWER COMMON INLET SCRUBBER LIQUOR
ANALYSIS RESULTS AT UNION OIL COMPANY, BREA, CALIFORNIA

					Measurements on Composite Samples	
Date	Run No.	Time	pH	Temperature (°F)	Urea (ppm)	Undissolved Solids (mg/l)
4-24-80	1	1430	8.60	83		
		1515	8.63	82		
		1600	8.60	82		
		1630	8.65	83		
		Average	8.62	83	24300	15.5
4-25-80	2	1000	8.33	80		
		1100	8.38	82		
		1130	8.30	80		
		1210	8.51	82		
		Average	8.38	81	22500	5.9
4-25-80	3	1330	8.58	82		
		1430	8.77	82		
		1510	8.40	81		
		1600	8.37	82		
		Average	8.53	82	24200	64.4

TABLE 2-6

AMBIENT AIR TEMPERATURE AND RELATIVE HUMIDITY MEASUREMENTS
DURING EMISSIONS TESTS AT UNION OIL COMPANY, BREA, CALIFORNIA

Run No.	Date	Time	Wet Bulb (°F)	Dry Bulb (°F)	Relative Humidity (%)
Prill Tower 2	4-25-80	1030	58	68	54
		1100	58	68	54
		1145	58	67	58
Prill Tower 3	4-25-80	1330	59	70.5	49.5
		1440	59	70	51
		1545	60	70	56
All 3 Prill Cooler Runs	4-28-80	1330	57.5	63.5	69.5
		1640	55.5	51.0	91

3.0 PROCESS DESCRIPTION AND OPERATION

3.1 Process Equipment

The urea manufacturing process consists of urea solution synthesis and prill tower solids production, and the process produces either feed grade or fertilizer grade urea. A flow diagram of the process is shown in Figure 3-1.

The urea solution leaving the synthesis process is at a concentration of about 75 percent. This solution then passes through two falling-film vacuum evaporators in series and is concentrated to 99.7 percent. From the evaporators the solution (urea melt) is pumped to a head tank at the top of the prill tower. The melt is sprayed from a spinning bucket and the melt droplets fall against a counter-current of ambient air drawn through the tower. As they fall, the droplets dry to form the solid urea granules (prills). The prills are removed from the bottom of the tower by a conveyor and are screened. Agriculture (fertilizer) grade product passes through a rotary drum cooler and is then transported to bulk storage; feed grade is brought directly to bulk storage. Offsize material is redissolved and reprocessed.

The prill tower operates 24 hours each day, 365 days per year and has an extended production capacity of about 370 tons/day for fertilizer grade product and 220 tons/day for feed grade product. The chemical process for both products are nearly the same. The prill tower operation is changed in order to produce the smaller sized feed granules.

At the top of the prill tower are four exhaust ducts, each equipped with a fan, and each controlled by a packed bed scrubber. While fertilizer grade prills are being produced, all four fans are in operation pulling air upward through the tower. Air enters the tower through louvers at the base of the prill tower. When feed grade prills are being produced, the fans are not

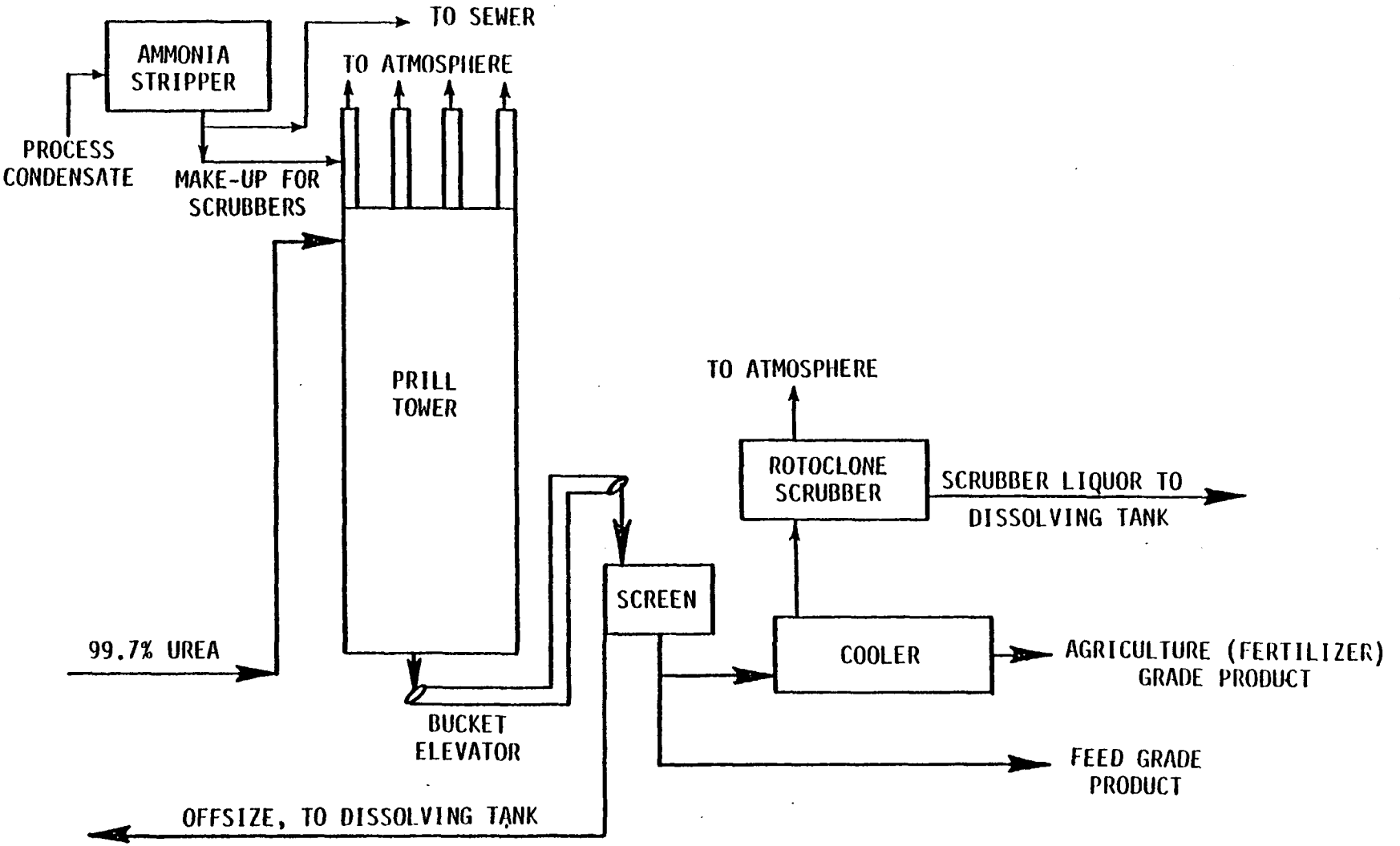

FIGURE 3-1: UREA MANUFACTURING PROCESS FLOW DIAGRAM
UNION OIL COMPANY OF CALIFORNIA
BREA, CALIFORNIA

operating but the louvers at the bottom of the tower are left open. Air flow in the tower results from natural convection: the air in the tower is heated by the falling prills and rises to be replaced by the cooler ambient air entering through the louvers.

The four scrubbers atop the 150-foot high prill tower operate simultaneously and consist of two sections: a low pressure spray section and a high pressure spray section. The scrubbers have a common sump and pumping system for collecting and recycling the scrubber liquor. These scrubbers were designed by Union Oil Company personnel and the design is considered proprietary.

The rotary drum cooler in the urea plant is used to supply the additional cooling required when agricultural prills are being produced. Prills are conveyed through the rotary cooler by means of a series of lifting flights. Air flow is countercurrent to prills and is induced by the Rotoclone mechanically-aided wet scrubber. Inlet air is conditioned to remove water vapor before introduction to the cooler.

3.2 Process Monitoring

During the emissions tests at the prill tower and prill cooler, a number of operating parameters were monitored to ensure that process and control equipment were operating normally. These parameters are shown in Tables 3-1 through 3-3. The numerical values of some parameters are considered confidential by the Union Oil Company. In order to indicate trends in magnitude of operating parameters during each run and between the runs without revealing confidential information, normalized values were calculated for these parameters. The normalized value is based on a deviation from a standard value. The standard value is an average value representative of normal operation at

TABLE 3-1

SUMMARY OF MONITORED PROCESS OPERATING PARAMETERS FOR THE UREA PRILL TOWER TESTS AT UNION OIL COMPANY, BREA, CALIFORNIA

Time[a] (Minutes)	Ammonia Feed Rate to Reactor[b]	Carbon Dioxide Feed Rate to Reactor[b]	75% Urea to 1st Stage Evaporator Flowrate[b]	Level in 75% Urea Storage Tank[b]	Temperature of Urea to Head Tank (°F)
Run 1					
-26	2.14	-4.80	.03	6.8	278
-11	.47	-3.65	.03	10.1	278
0	.47	-3.65	.03	13.4	278
4	.47	-3.08	.03	16.8	278
19	.47	-2.50	.03	20.1	278
34	.47	-4.23	.03	26.8	278
49	.47	-4.23	.03	30.1	278
64	1.02	-4.23	.03	33.4	278
79	1.58	-4.23	.03	40.1	277
94	1.58	1.51	.03	43.5	278
109	1.58	1.51	.03	46.8	276
124	-.09	2.66	.60	46.8	280
139	-.09	2.66	1.75	46.8	279
149	-.09	2.66	1.75	46.8	278
Run 2					
-30	-2.88	-5.37	.03	13.43	279
-15	-2.88	-5.37	.03	6.76	279
0	-2.88	-5.37	.03	-3.25	279
15	-2.88	-5.37	.03	-13.26	279
30	-.65	-5.37	.03	26.6	279
48	-.65	-5.37	.03	33.3	279
60	-.65	-5.37	.03	-40.0	279
75	-.65	-5.37	.03	-36.6	279
90	-.65	-3.65	.03	-36.6	278
105	-.65	-.78	.03	36.6	278
120	-.65	-2.66	.03	36.6	278
135	-.65	-2.66	.03	-36.6	278
150	-.65	-2.66	.03	-36.6	279

TABLE 3-1 (Continued)

SUMMARY OF MONITORED PROCESS OPERATING PARAMETERS FOR THE UREA PRILL TOWER TESTS AT UNION OIL COMPANY, BREA, CALIFORNIA
(Continued)

Time[a] (Minutes)	Ammonia Feed Rate to Reactor[b]	Carbon Dioxide Feed Rate to Reactor[b]	75% Urea to 1st Stage Evaporator Flowrate[b]	Level in 75% Urea Storage Tank[b]	Temperature of Urea to Head Tank (^{o}F)
Run 3					
-15	-.09	-4.95	.03	-26.6	286
0	-.09	-4.38	.03	-23.3	279
15	-.09	-4.38	.03	-19.9	281
30	-.09	-4.38	2.89	-16.6	279
45	-.09	-4.38	2.32	-13.3	280
60	-.09	-4.38	1.18	-9.9	278
75	-.09	-4.38	.60	-6.6	278
90	-.09	-3.80	.60	-6.6	278
105	-.09	-2.66	.60	-6.6	278
120	-.09	2.66	.32	-6.6	279
135	-.09	2.66	.03	-6.6	277
150	-.09	2.66	.03	-6.6	279

[a]Dates and times corresponding to t = 0 were as follows: Run 1 - 4/24/80, 1426
Run 2 - 4/25/80, 0945
Run 3 - 4/25/80, 1330

[b]Values reported as % deviation from standard value = $[(x_t - x_s)/x_s]x100$

TABLE 3-2

SUMMARY OF MONITORED PROCESS OPERATING PARAMETERS
FOR THE UREA PRILL TOWER EMISSION CONTROL EQUIPMENT
AT UNION OIL COMPANY,
BREA, CALIFORNIA

Time[a] (Minutes)	Scrubber Liquor Make Up Flowrate[b]	High Pressure Spray Flowrate[b]	Low Pressure Spray Flowrate[b]
Run 1			
-11	4.93		
0	4.93		
4	4.93	0	.87
34	6.01	0	.87
64	2.76	0	.87
94	8.17	0	-.68
124	3.85	0	.87
154	4.93	0	.87
Run 2			
-15	-1.56		
0	.48	0	-.68
45	-1.56	0	-.68
75	-1.56	0	-.68
105	-1.56	0	-.68
135	-.48	0	-.68
Run 3			
-15	-4.81		
0	-1.56	0	-.68
30	-6.97	0	-.68
60	-4.81	0	-.68
90	-4.81	0	.87
120	-5.89	0	.87

[a]Dates and times corresponding to t = 0 were as follows: Run 1 - 4/24/80, 1426
Run 2 - 4/25/80, 0945
Run 3 - 4/25/80, 1330

[b]Values reported as % deviation from standard value = $[(x_t - x_s)/x_s]x100$

TABLE 3-3

SUMMARY OF MONITORED PROCESS OPERATING PARAMETERS FOR THE UREA ROTARY DRUM COOLER TESTS AT UNION OIL COMPANY, BREA, CALIFORNIA

Time (Minutes)	Ammonia Feed Rate to Reactor[b]	Carbon Dioxide Feed Rate to Reactor[b]	75% Urea to 1st Stage Evaporator Flowrate[b]	Level to 75% Urea Storage Tank[b]	Temp. Air Into Cooler (°F)	Temp. Product from Prill Tower (°F)	Temp. Product from Cooler (°F)
Run 1							
-14	-.65	-1.36	-.83	.08	64	157	123
0	.47	-1.36	-.83	.08	64		
16	.47	-1.36	-.83	.08	65		
31	.47	-1.36	-.83	.08	64		
46	.47	-1.36	-.83	.08	64		
61	.47	-1.36	-.83	.08			
76	.47	-1.36	-.83	.08	78		
91	.47	.94	-.83	.08	76	195	139
Run 2							
-25	-.09	.36	-.25	3.42			
0	-.09	.36	-.25	3.42	73		
20	-.09	.36	-.25	3.42			
35	-.09	.36	-.25	3.42	74		
50	-.09	.36	-.25	3.42			
65	-.09	.36	-.25	3.42	72		
80	-.09	.36	-.25	3.42		183	134
95	-.09	.36	-.25	3.42	71		
110	-.09	.36	-.25	3.42			
Run 3							
-13	-.09	.36	-.25	3.42			
0	-.09	.36	-.25	3.42	71		
17	-.09	-.21	.03	3.42			
32	-.47	-.21	.03	3.42	70		
47	-.47	-.21	.03	3.42		191	136
62	-.47	-.21	.03	3.42	72		
77	-.47	.36	.03	3.42			
92	-.47	.94	.03	3.42	72		
99	-.47	.94	.03	3.42			

[a]Dates and times corresponding to t = 0 were as follows: Run 1 - 4/28/80, 1214
Run 2 - 4/28/80, 1640
Run 3 - 4/28/80, 1913

[b]Values reported as % deviation from standard value = $[(x_t - x_s)/x_s]x100$

the operating capacity during the tests. These normalized values were calculated by subtracting the standard value of a parameter from the value for the parameter at a given time and dividing by the standard value.

Actual and normalized values for process operating parameters monitored during prill tower testing are reported in Table 3-1. Normalized values for operating parameters of the Northeast scrubber during prill tower testing are reported in Table 3-2. Standard values for these parameters are contained in the confidential files.

Synthesis process parameters (carbon dioxide flowrate to reactor and ammonia flowrate to reactor) were recorded as indicators of overall urea production. The flowrate of 75 percent urea to the first evaporator was used as an indicator of urea melt and solids production. Changes in the level of the 75 percent urea storage tank accompanied changes in the urea synthesis process. The temperature of the urea melt pumped to the head tank was also used as an indicator of normal operation.

During the prill tower emissions tests scrubber liquor samples were collected and analyzed for urea and solids content, as well as temperature and pH, in order to characterize variations in the scrubber liquor during each test run. Pressure drops were monitored periodically and were constant at about 2.5 inches water. Although formal visible emissions observations were not made during these emissions tests, scrubber outlet opacities were estimated to range between 5 and 10 percent, depending on time of day.

Actual and normalized values for process operating parameters monitored during the cooler emissions tests are shown in Table 3-3. Standard values for these parameters are contained in the confidential files. Inlet air and product temperatures were used as indicators of stable cooler operations

During Cooler Run 1 on April 28, 1980, there was a shift in the inlet air temperature resulting from an increase in steam flow to the air preconditioning system. This had no apparent effect on cooler outlet air temperature.

During the first traverse of Cooler Run 2, the air flow was noticeably reduced from the previous velocity traverses. The lower air flow was the result of caking in the outlet duct from the control device. This duct was cleaned before continuing with the final traverse for Cooler Run 2. Thus, the overall average air flowrate for Cooler Run 2 was lower than for the other two cooler tests. Washing out cooler ducts is a standard practice at this urea plant.

3.3 General Plant Operations

Operating conditions and production rates during tests are summarized in Table 3-4. Based upon observations of pertinent operating parameters, all 3 tests on the prill tower are representative of normal conditions. Test 2 on the rotary drum cooler is expected to show a slightly reduced air flow rate. However, this should be considered representative of normal operations.

TABLE 3-4

SUMMARY OF OPERATING CONDITIONS AND PRODUCTION RATES AT
UNION OIL COMPANY, BREA, CALIFORNIA

	Prill Tower			Prill Cooler		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Production Rate[a] (percent capacity)	>90	>90	>90	>89	>89	>89
Anomalies in Operations	None	None	None	None	airflow reduced[b]	none

[a]Production rates are approximations
[b]Caking in outlet duct during first traverse

PRODUCTION RATES OF UREA PRILLING DURING EMISSIONS TESTING

24-28 April 1980

Test Location	Date	Time Period of Test	Production Rate (tons per day)
Prill Tower	24 April 1980	2:26 pm - 4:55 pm	289
Prill Tower	25 April 1980	9:45 am - 12:15 pm	300 (8:00 am)
Prill Tower	25 April 1980	1:30 pm - 4:00 pm	295 (1:00 pm)
Prill Cooler	28 April 1980	12:14 pm - 1:45 pm	280 (12 Noon)
Prill Cooler	28 April 1980	4:40 pm - 6:30 pm	280 (4:00 pm)
Prill Cooler	28 April 1980	7:13 pm - 8:52 pm	280 (7:00 pm)

4.0 LOCATION OF SAMPLING POINTS

Four fiberglass scrubbers are located atop the prill tower at the Union Oil Company facility. All four scrubbers are of similar design and construction. The scrubber located on the Northeast corner of the prill tower was recommended for testing by Union Oil personnel. An overhead schematic of the four scrubber outlet stacks is shown in Figure 4-1.

4.1 Prill Tower Scrubber Outlet (Northeast Stack)

The cleaned gases exiting the scrubber unit pass through a 4-foot section of 47-inch I.D. duct and then to the atmosphere. This duct was fitted with two 4-inch I.D. pipe-flange sampling ports positioned 90 degrees apart in a horizontal plane. The ports were located 24 inches downstream from a duct transition and 24 inches upstream from the duct discharge. Since these port locations did not meet the "eight and two diameters" criteria of EPA Reference Method 1, 24 sampling points were chosen for each traverse axis, for a total of 48 sampling points as specified by Method 1. Figure 4-2 shows a schematic of the scrubber and sampling locations. Figure 4-3 shows a cross-sectional view of the outlet duct at the sampling location and lists the exact distance of each sampling point from the outside flange edge.

4.2 Prill Cooler Scrubber Inlet

Sampling for urea particulate was conducted at the inlet of the prill cooler rotoclone scrubber in a 24-inch I.D. steel duct. A schematic of the sampling location is shown in Figure 4-4.

The inlet duct was fitted with two 3-inch I.D. pipe-flange sampling ports positioned 90 degrees apart in a vertical plane. The nearest upstream disturbance was an in-line damper located 55 inches from the ports. The

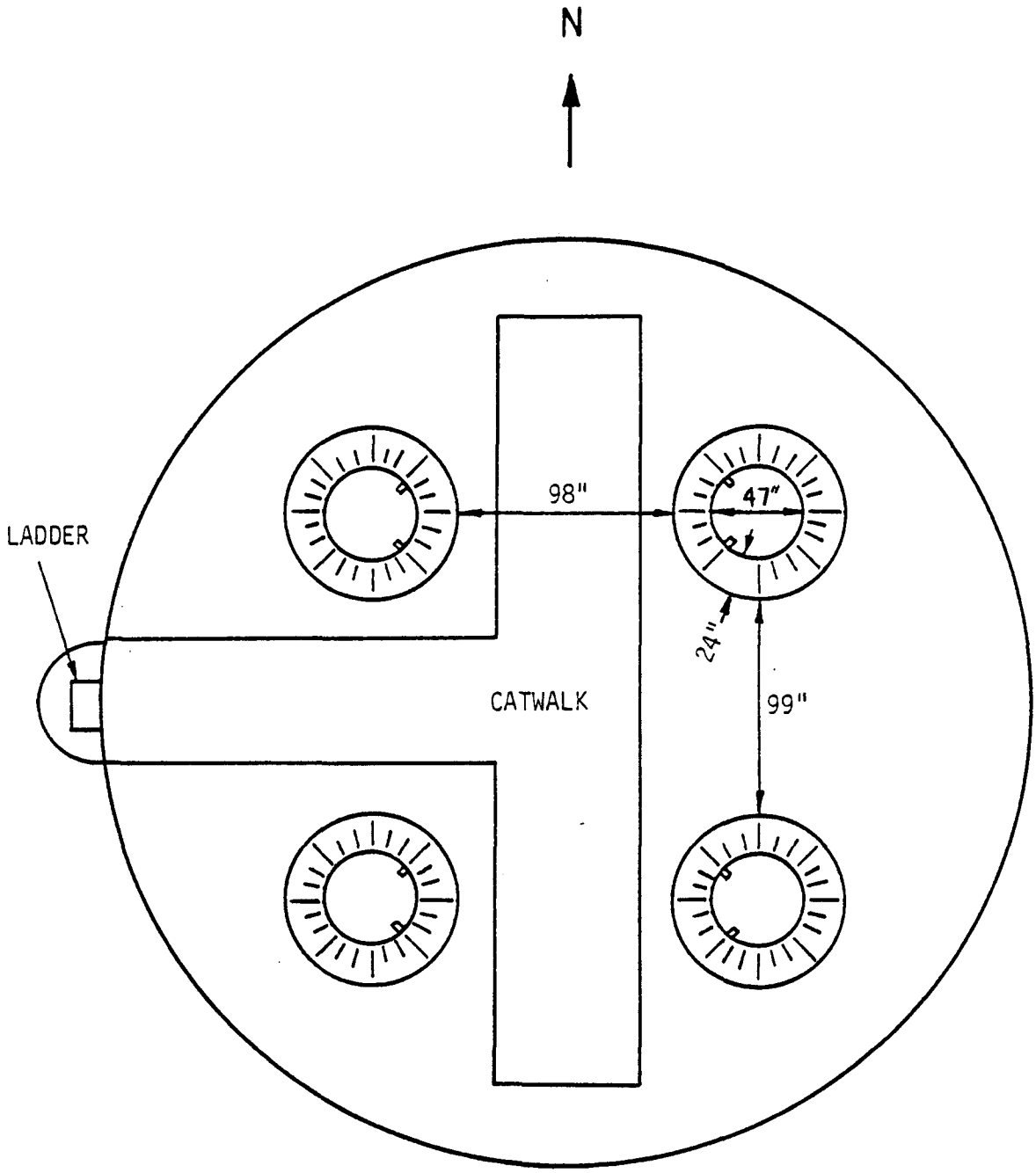

FIGURE 4-1: OVERHEAD SCHEMATIC OF PRILL TOWER SCRUBBER OUTLETS AT UNION OIL COMPANY, BREA, CALIFORNIA.

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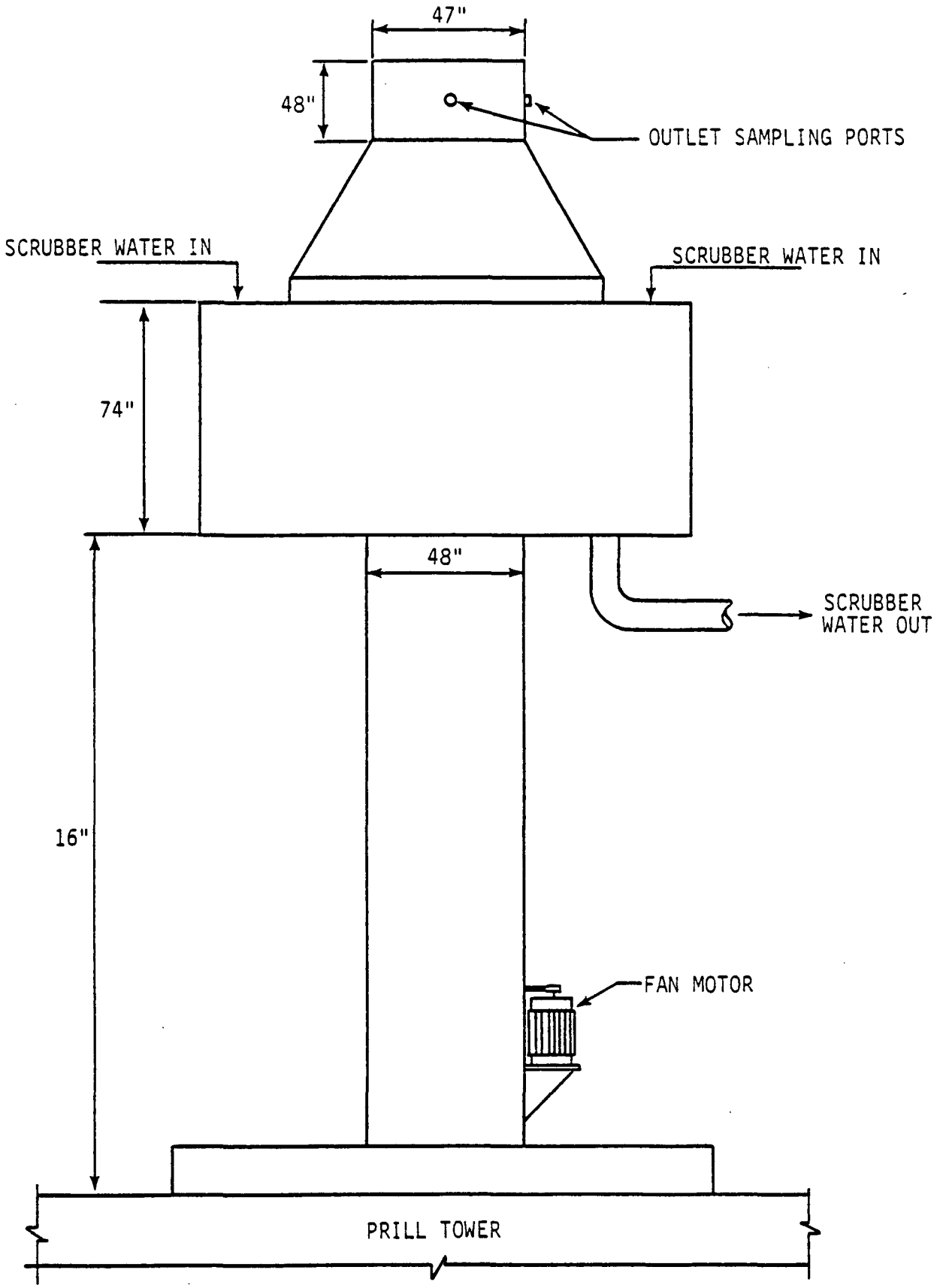
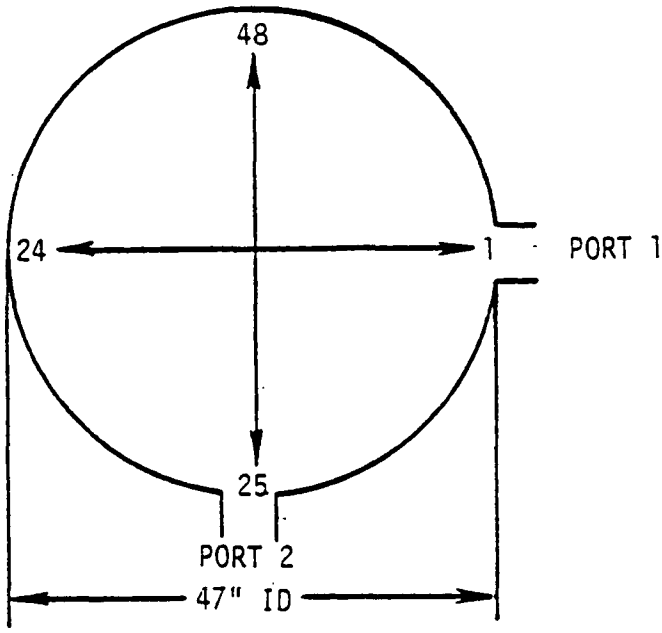


FIGURE 4-2: UREA PRILL TOWER SCRUBBER
UNION OIL COMPANY,
BREA, CALIFORNIA



TRAVERSE POINT NO.	TRAVERSE POINT LOCATION FROM OUTSIDE FLANGE (IN.)
1	3-1/2
2	3-1/2
3	4-1/2
4	5-3/4
5	7
6	8-1/2
7	9-1/2
8	11
9	12-3/4
10	14-3/4
11	17
12	20-3/4
13	30-1/4
14	34
15	36-1/4
16	38
17	40
18	41-1/2
19	42-3/4
20	44
21	45-1/4
22	46-1/2
23	47-1/2
24	47-1/2

FIGURE 4-3: LOCATION OF SAMPLING POINTS IN UREA PRILL TOWER SCUBBER OUTLET UNION OIL COMPANY, BREA, CALIFORNIA.

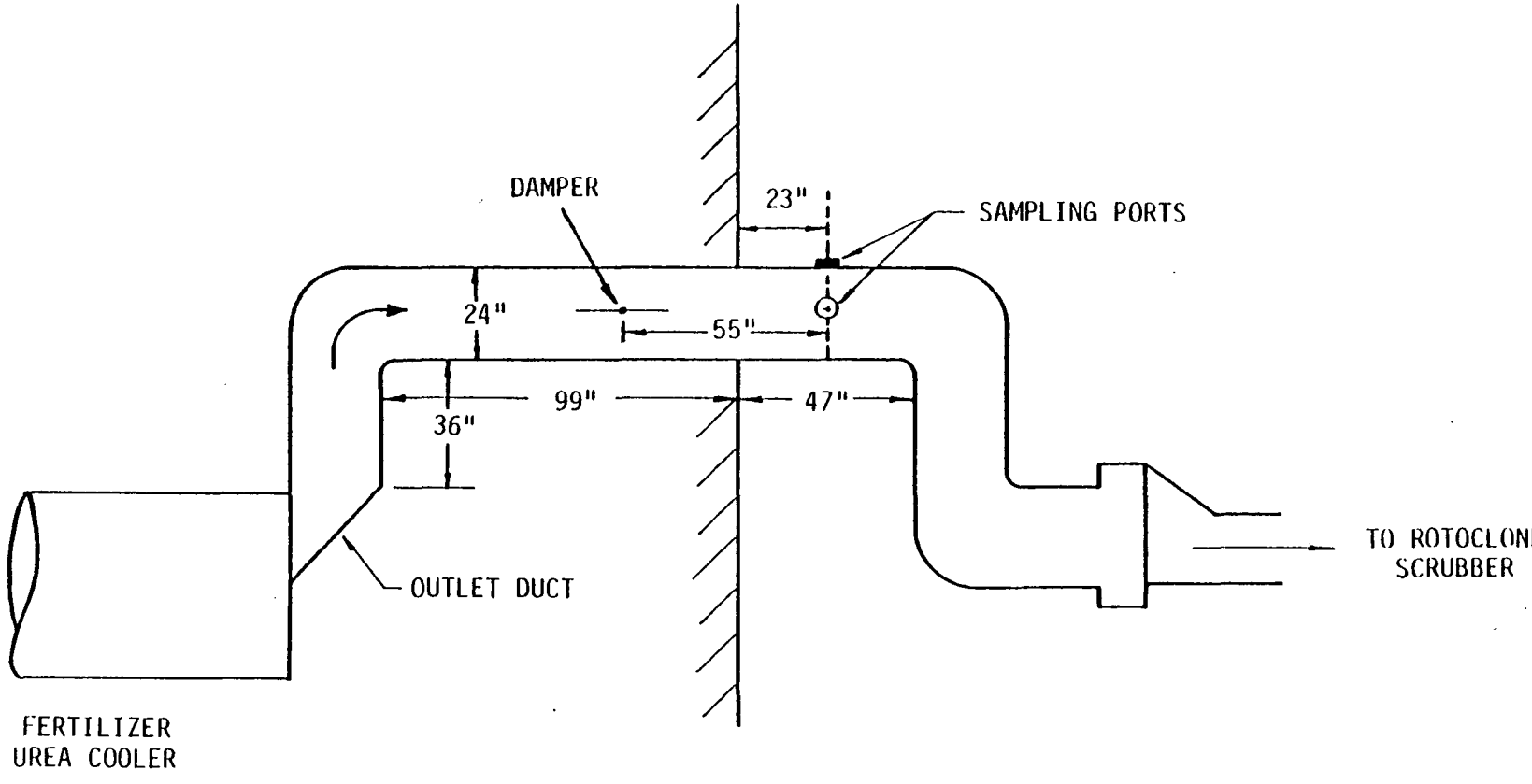


FIGURE 4-4: PRILL COOLER SCRUBBER INLET SAMPLING SITE AT UNION OIL COMPANY, BREA, CALIFORNIA.

0988-017

nearest downstream disturbance was a short-radius 90 degree bend 47 inches from the ports. The "eight and two diameters criteria" could not be met, hence 16 sampling points were chosen for each traverse axis, for a total of 32 sampling points as specified by EPA Reference Method 1. Figure 4-5 shows a cross-sectional view of the cooler inlet duct at the sampling location and the exact distance of each sampling point from the outside flange edge.

4.3 Scrubber Liquor Common Inlet Sampling Location

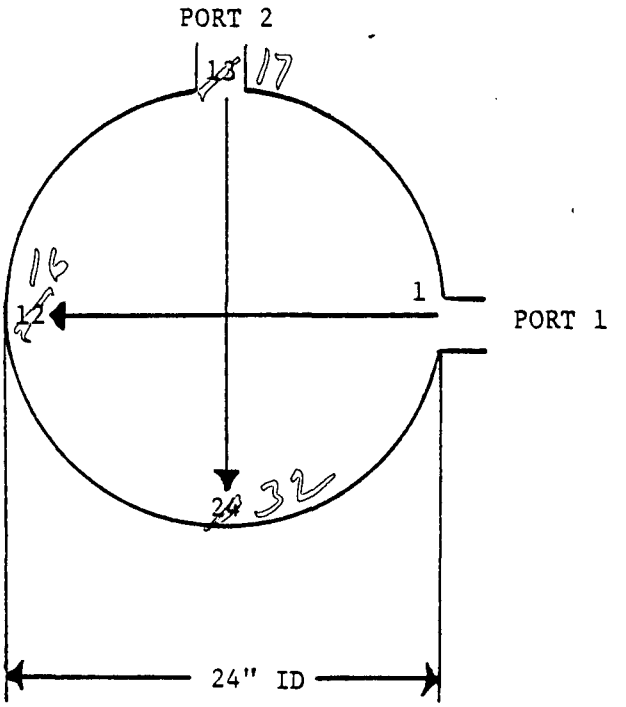
The prill tower scrubber liquor collects in a common sump and is then circulated to the four scrubbers through two pump systems: a high pressure system and a low pressure system. The scrubber liquor samples were taken from an existing valve downstream from the circulating pump. Figure 4-6 shows the location of this sampling site.

4.4 Velocity Traverse Measurement Locations

Velocity head and temperature measurements were made in the three prill tower scrubber outlets not tested for emissions. These measurement locations were identical to the sampling location in the Northeast scrubber outlet as shown in Figures 4-2 and 4-3.

4.5 Ambient Air Temperature and Relative Humidity Measurement Location

Ambient air temperature and relative humidity measurements were made periodically during the emissions testing program from a location near the base of the prill tower. This location was approximately 30 feet from the Northwest side of the prill tower directly across from one of the tower air inlets.



TRAVERSE POINT NO.	TRAVERSE POINT LOCATION FROM OUTSIDE FLANGE (IN.)
1	2-3/4
2	3
3	3-3/4
4	4-3/4
5	5-3/4
6	7
7	8-1/2
8	10-1/2
9	16-1/2
10	18-3/4
11	20-1/4
12	21-1/2
13	22-1/2
14	23-1/2
15	24-1/4
16	24-1/2

FIGURE 4-5: LOCATION OF SAMPLING POINTS IN PRILL COOLER INLET AT UNION OIL COMPANY, BREA, CALIFORNIA.

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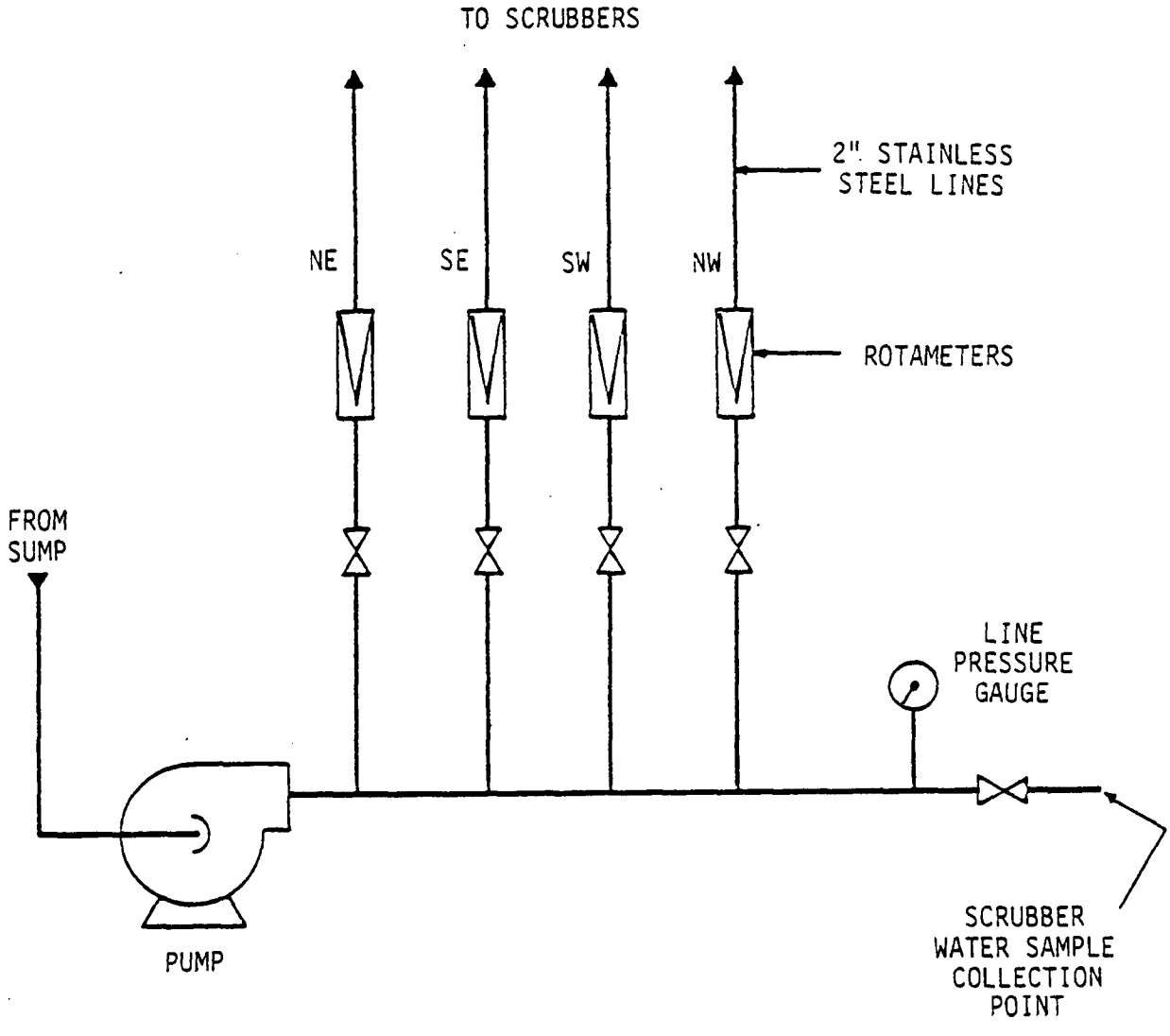

FIGURE 4-6: UREA PRILL TOWER SCRUBBER LIQUOR SAMPLING LOCATION AT UNION OIL COMPANY, BREA, CALIFORNIA.

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4.6 Pressure Drop Measurement Location

Pressure drops across the prill tower Northeast scrubber were made with a vertical U-tube water manometer. One side of the manometer was connected to a pressure tap inserted into the scrubber inlet duct approximately 12 feet below the scrubber. The other side of the manometer was open to the atmosphere.

5.0 SAMPLING AND ANALYSIS METHODS

This section presents general descriptions of sampling and analysis procedures employed during the emissions testing program conducted at the Union Oil Company, Brea, California urea manufacturing facility during April 24-28, 1980. Details of sampling and analysis procedures are contained in Appendices E and F.

5.1 EPA Reference Methods Used in This Program

The following EPA Reference Methods were used during this emission testing program. These methods are taken from "Standards of Performance for New Stationary Sources", Appendix A, Federal Register, Volume 42, No. 160, Thursday, August 18, 1977, pp 41755 ff.

- Method 1 - Sample and Velocity Traverses for Stationary Sources

  This method specifies the number and location of sampling points within a duct, taking into account duct size and shape and local flow disturbances.

- Method 2 - Determination of Stack Gas Velocity and Volumetric Flowrate

  This method specifies the measurement of gas velocity and flowrate using a pitot tube, manometer and temperature sensor. The physical dimensions of the pitot tube and its spatial relationship to the temperature sensor and any sample probe are also specified.

- Method 4 - Determination of Moisture Content in Stack Gases

  This method describes the extraction of a gas sample from a stack and the removal and measurement of the moisture in that sample by condensation impingers. The assembly and operation of the required sampling train is specified.

The emissions tests and sample analyses were performed using EPA Reference Method 28, Determination of Particulate (Urea) Emissions from Urea Plants. This method incorporates modifications to EPA Reference Method 5, Determination of Particulate Emissions from Stationary Sources, that reflect the char-

acteristics of urea and urea sources. With Method 5 as a reference, Method 28 specifies the isokinetic sampling of urea particulate from a gas stream utilizing techniques introduced in Methods 1, 2, and 4. Sample collection and recovery, sampling train cleaning and calibration, and gas stream flowrate calculations procedures are specified. No filter is used in the sampling train. Analysis of impinger samples for urea is performed with the p-dimethylaminobenzaldehyde method. Method 28 is described in its entirety in Appendix E.

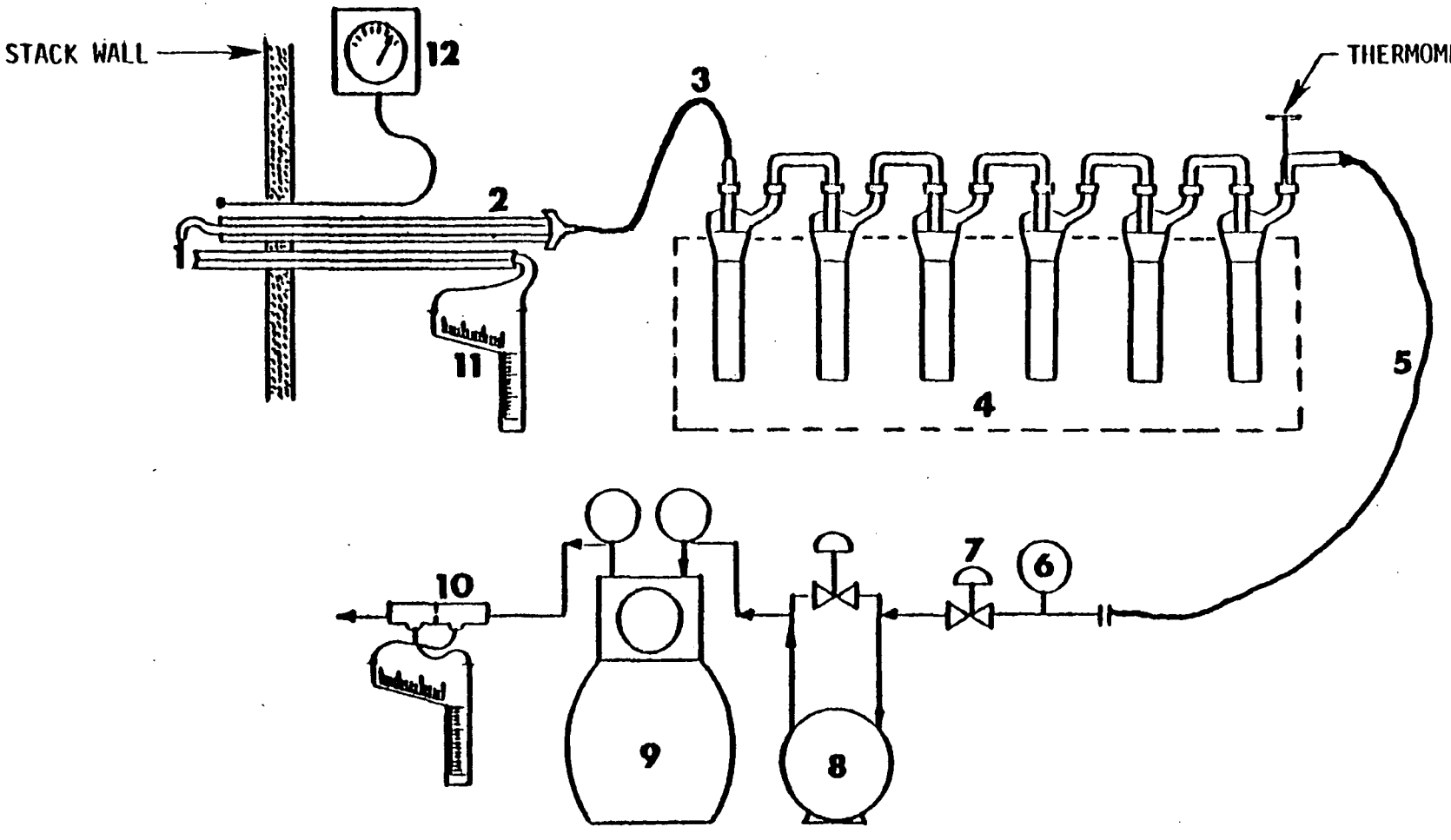
5.2 Urea Sampling and Analysis at the Prill Tower Northeast Scrubber and Prill Cooler Scrubber

5.2.1 Sampling Methods

Urea and ammonia in the outlet gas stream of the prill tower Northeast scrubber and inlet gas stream of the prill cooler scrubber were sampled at points located in accordance with EPA Method 1. Duct gas velocities were measured using S-type pitot tubes constructed and calibrated in accordance with EPA Method 2.

The sampling train used on this program is shown in Figure 5-1 and is a modification to the particulate sampling train specified in EPA Method 28. The modifications used were: two water impingers (instead of three), two acid impingers (instead of one), use of an empty impinger, and use of a Teflon line. No filter is used in the sampling train.

The sampling train shown in Figure 5-1 consists of a nozzle, probe, Teflon line, six impingers, vacuum pump, dry gas meter, and an orifice flow meter. The nozzle is stainless steel and of buttonhook shape. The nozzle was connected to a 5/8-inch stainless steel glass-lined probe wrapped with nichrome heating wire and jacketed. Following the probe, the gas stream passed through a 3/8-inch I.D. teflon line into an ice bath/impinger system. The impinger system consisted of six impingers in series. The first, third, fifth and



LEGEND

1 - NOZZLE	7 - NEEDLE VALVE
2 - PROBE	8 - PUMP
3 - TEFLON LINE	9 - DRY GAS METER
4 - ICE BATH	10 - ORIFICE
5 - FLEXIBLE LINE	11 - PITOT TUBE & INCLINED MANOMETER
6 - VACUUM GAGE	12 - POTENTIOMETER

FIGURE 5-1: MODIFIED EPA PARTICULATE SAMPLING TRAIN

sixth impingers were the Greenburg-Smith design, modified by replacing the tip with a one-half inch glass tube extended to within one-half inch of the impinger bottom. The second and fourth impingers were of regular Greenburg-Smith design including tips with orifice plates located within one-half inch of the impinger bottom. The first two impingers contained deionized, distilled water (100 mls each). The next two impingers contained 1N H_2SO_4 (100 mls each). The fifth impinger was empty, and the sixth contained 200 grams of indicating silica gel. Leaving the last impinger, the sample stream flowed through flexible tubing, a vacuum gauge, needle valve, pump, and a dry gas meter. A calibrated orifice and inclined manometer completed the train. The stack velocity pressure was measured using a pitot tube and inclined manometer. Stack temperature was monitored by a thermocouple attached to the probe and connected to a potentiometer. A nomograph was used to determine the orifice pressure drop required for any pitot velocity pressure and stack temperature in order to maintain isokinetic sampling conditions.

The probe temperature was maintained at about $10^{\circ}F$ above the stack gas temperature in order to prevent condensation within the probe.

Test data recorded at each sampling point included test time, sampling duration at each traverse point, pitot pressure, stack temperature, dry gas meter volume and inlet-outlet temperature, probe temperature and orifice pressure drop.

The only significant sampling problem occurred at the prill cooler scrubber inlet. The test runs were frequently interrupted by pitot tube tip plugging due to the heavy particulate loading. Because of this problem, test run 1 at the prill cooler scrubber inlet was performed utilizing the velocity head readings obtained from the preliminary velocity traverse. During test runs 2 and 3, the pitot was blown clear with compressed air each time it plugged.

5.2.2 Sample Recovery and Preparation

Prill Tower Samples

At the completion of each test run, the train was leak checked. Then the nozzle, probe and flexible Teflon line were washed with deionized, distilled water (three times). The volume of the contents of each impinger was measured, and the samples were put in glass containers with Teflon-lined caps as follows:

Jar #1 - nozzle, probe, and Teflon line washes.

Jar #2 - contents of the first impinger and the distilled water wash of the impinger and its glassware connector.

Jar #3 - contents of the second impinger and the distilled water wash of the impinger and its glassware connector.

Jar #4 - contents of the third, fourth, and fifth impingers and the 1N H_2SO_4 wash of these impingers and their connecting glassware.

Jar #5 - silica gel from the sixth impinger.

These sample containers were then returned to TRC for urea and ammonia analysis. Only jars 1 and 2 in run 1 contained some rust-colored particulate matter, possibly pipe scale, which was filtered out before sample analysis. All other samples were clear.

Prill Cooler Samples

At the completion of each test run the train was leak checked. Then the nozzle, probe and flexible Teflon line were washed with deionized, distilled water (three times). Samples were put in glass containers with Teflon-lined caps, as follows:

Jar #1 - contents of the first two impingers, and the deionized, distilled water wash of their connecting glassware and the nozzle, probe and Teflon line.

Jar #2 - contents of the third, fourth, and fifth impingers and the 1N H_2SO_4 rinse of the impingers and their connecting glassware.

Jar #3 - silica gel from the sixth impinger.

These sample containers were returned to TRC for urea and ammonia analysis. Rust-colored particulate matter was noted in the Jar 1 samples from test runs 2 and 3. These samples were filtered prior to analysis.

5.2.3 Sample Analysis

All samples were analyzed at the TRC laboratory within 20 days after collection. At TRC, the volume of the contents of each sample jar was measured.

Each individual water sample (jars 1, 2, and 3 for the prill tower and jar 1 for the prill cooler) was analyzed for urea with the p-dimethylaminobenzaldehyde (PDAB) method with preliminary distillation. For the urea analysis, a sodium borate buffer and NaOH were added to each sample to adjust the pH to 9.5 or greater. The samples were then boiled to remove ammonia and the PDAB color reagent was added to the residue. The solution absorbances were then measured in a spectrophotometer.

The acid samples (jar 4 for the prill tower and jar 2 for the prill cooler) were analyzed for urea by the same PDAB method. An additional 1 ml concentrated hydrochloric acid per liter of sample was added to acid impinger sample solutions prior to the absorbance readings to remove the turbidity that resulted upon addition of the PDAB color reagent.

Urea standards were prepared with the same acid content as the samples. Sample absorbances were converted to urea concentration with the calibration curve drawn from the analysis of these standards.

5.3 Ammonia Sampling and Analysis at the Prill Tower Northeast Scrubber and Prill Cooler Scrubber

5.3.1 Sampling, Sample Recovery and Preparation

The same samples collected and recovered as described in Sections 5.2.1 and 5.2.2 were analyzed for ammonia as well as urea.

5.3.2 Sample Analysis

The water portions and the acid portions were analyzed for ammonia content by the specific ion electrode (SIE) method. An Orion model 95-10 ammonia electrode was used in accordance with the electrode manufacturer's procedures. This method is extremely specific for ammonia and is subject to few, if any, interferences. All ammonia analyses were performed at the TRC laboratory within 20 days of collection.

5.4 Northeast Scrubber Liquor Sampling and Analysis

Four 100-ml liquor samples were collected during each of the emission test runs at the prill tower scrubber outlet. The temperature of each liquor sample was measured immediately following its collection. Once the sample reached room temperature, the pH was measured. The samples collected during a test run were then combined to form one composite sample per run.

At the TRC laboratory, the composite samples were filtered using a tared glass fiber filter in order to remove undissolved material. The urea analysis was performed using the PDAB method as discussed in Section 5.2.3. The solids analysis was performed by desiccating and weighing the filter to a constant weight.

5.5 Volumetric Flowrate Measurements in the Northwest, Southeast, and Southwest Scrubber Outlets

Velocity traverses were performed at the Northwest, Southeast, and Southwest scrubber outlets before and after each emission test run at the

Northeast scrubber outlet. Two perpendicular traverses were performed at each outlet during each velocity test, with velocity head and stack gas temperature measured at each sampling point, in accordance with EPA Reference Method 2.

The duct static pressure and percent moisture values obtained from the Northeast outlet were applied on a run-by-run basis to the other three outlets in order to compute volumetric flowrates. Velocity head and temperature measurement data are contained in Appendix C.

5.6 Ambient Air Temperature and Relative Humidity

Ambient air temperature and relative humidity were recorded periodically at the base of the prill tower during the emission testing program. Wet bulb and dry bulb temperature measurements were made with a Bendix psychron. Psychrometric tables were then used to compute relative humidity from these measurements.

5.7 Pressure Drop Measurements Across the Northeast Scrubber

Pressure drop measurements across the prill tower Northeast scrubber were observed but not recorded. During the first test run, it was apparent that the pressure drop was very small and very steady. Under the direction of the Technical Manager the pressure drop readings were monitored during each test run. One side of a vertical U-tube water manometer was connected to a pressure tap inserted into the scrubber inlet duct approximately 12 feet below the scrubber. The other side of the manometer was open to the atmosphere.